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Factors affecting metal releases from contaminated marine sediments

Dianne F. Jolley
University of Wollongong, djolley@uow.edu.au

Clare A. Atkinson
University of Wollongong, clareatk@uow.edu.au

Stuart L. Simpson
CSIRO, stuart.simpson@csiro.au

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Abstract

In aquatic environments, the depth of oxygen penetration into sediment depends on sediment texture, porosity, permeability and the extent of biological (e.g., bioturbation) and physical (e.g., wave action) processes. Below the oxygen penetration depth (generally 10 mm) anoxic conditions prevail and bacteria use other oxidants such as iron and manganese oxides and sulfate to breakdown organic matter. The bacteria-catalysed reduction of sulfate releases hydrogen sulfide according to Equation 1. The release of H2S into the pore waters SO42- + bacteria → H2S (Equation 1).

Keywords

marine, contaminated, affecting, sediments, releases, factors, metal, CMMB

Disciplines

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Factors Affecting Metal Releases from Contaminated Marine Sediments

Dianne F. Jolley[1], Clare A. Atkinson[1], Stuart L. Simpson[2]

[1]GeoQuEST, Department of Chemistry, University of Wollongong NSW 2500, AUSTRALIA (djolley@uow.edu.au; caa99@uow.edu.au)
[2]Centre for Environmental Contaminants Research, CSIRO, Division of Energy Technology, Private Mailbag 7, Bangor, NSW 2234, AUSTRALIA (stuart.simpson@csiro.au)

INTRODUCTION

In aquatic environments, the depth of oxygen penetration into sediment depends on sediment texture, porosity, permeability and the extent of biological (e.g., bioturbation) and physical (e.g., wave action) processes. Below the oxygen penetration depth (generally 10 mm) anoxic conditions prevail and bacteria use other oxidants such as iron and manganese oxides and sulfate to breakdown organic matter. The bacteria-catalysed reduction of sulfate releases hydrogen sulfide according to Equation 1. The release of H_2S into the pore waters

$$SO_4^{2-} + \text{bacteria} \rightarrow H_2S \qquad \textbf{(Equation 1)}$$

enables a further reaction with dissolved metals forming highly insoluble reactive metal sulfides, the most dominant being iron monosulfide (FeS) (Simpson *et al.*, 2000). Trace metals under anoxic conditions react with this reactive sulfide fraction (FeS, measured as acid-volatile sulfide, AVS) to form insoluble sulfide phases (Di Toro *et al.*, 1992; Simpson *et al*, 2000), as per Equation 2. If concentration of sediment AVS is greater than the sum of

$$Me_{(aq)}^{2+} + FeS_{(s)} \rightarrow MeS_{(s)} + Fe_{(aq)}^{2+} \qquad \textbf{(Equation 2)}$$

Where Me = Cu, Cd, Pb, Zn, Se, Ni, etc.

metal concentrations, the sediment metals will become trapped as insoluble metal-sulfide complexes that are not biologically available. However, when the ratio of AVS:metals is low, high concentrations of metals may be present in the porewaters. Hence, sediments are not a permanent sink for metals. Metals can be released from sediments because of changes in physicochemical conditions, induced by factors such as overlying water chemistry and bioturbation. In this study the effect of altering the overlying water pH (pH 5.5, pH 7.0, pH 8.0), dissolved oxygen (DO) (3.0, 6.0, 8.0 mg/L) and salinity (15, 25 and 35 ‰), and the presence of bioturbating bivalves (*Tellina deltoidalis*) on the Cd, Cu, Pb and Zn release from metal contaminated marine sediments was monitored for 21 days. After this test period and bivalve removal, the sediment was disturbed and its impact monitored for 2-7 days.

METHODS

Metal contaminated sediments were collected from a marine barrier lake, coarse sieved (<2 mm) to remove debris, and fully characterised for pH, redox potential, AVS, TOC, pore water metals. The sediments were particle sized (<63 μm, 63 – 250 μm, > 250 μm) and the fractions analysed for total acid extractable and weak acid extractable metals. Test sediments were placed in containers with clean overlying seawaters, fitted with aeration and mixing systems, and sampled regularly. The affects of overlying water pH, dissolved oxygen, salinity and sediment bioturbation on overlying water Cu, Cd, Pb and Zn were measured.

RESULTS AND DISCUSSION

Metal release from sediments increased as pH decreased with a maximum release at pH 5.5 for copper, zinc (Figure 1a), cadmium and lead. A greater release of metals was observed

when sediments were disturbed on day 21, producing overlying water concentrations of 49 and 1570 μg/L for cadmium and zinc in undisturbed systems, compared to 92 and 2579 μg/L, respectively, after sediment disturbance. pH governs metal partitioning, where a decrease in pH increases the solubility of metal complexes, and as such metals will be released more rapidly from the sediment. Low pH and dissolved oxygen in overlying waters will also decrease the oxidation rate of the dissolved Fe(II)/Mn(II) released from sediments. A decrease in the rate of Fe(II)/Mn(II) oxidation will decrease the rate of metal precipitation from overlying waters as oxides of Fe and Mn, resulting in a net increase in dissolved metals in the overlying water.

There was little detectable metal release for the different dissolved oxygen (Figure 1b, zinc) and salinities, as these tests were carried out at natural seawater pH (8.0), where most metals are adsorbed or precipitated as insoluble complexes. The presence of the bioturbating bivalve *T. deltoidalis* appeared to slightly reduce metal release as sediments were oxidised at depth by bivalve burrowing, causing dissolved metals in porewaters to be sequestered by freshly oxidised insoluble precipitates (Fe/Mn oxyhydroxides). Resuspension induced a range of different responses depending on the test. Some displayed an immediate spike of metal release, whilst others showed a decrease in dissolved metal concentration followed by a release spike, before returning to near or just above pre-disturbance concentrations. This presentation will discuss the detailed findings of this study.

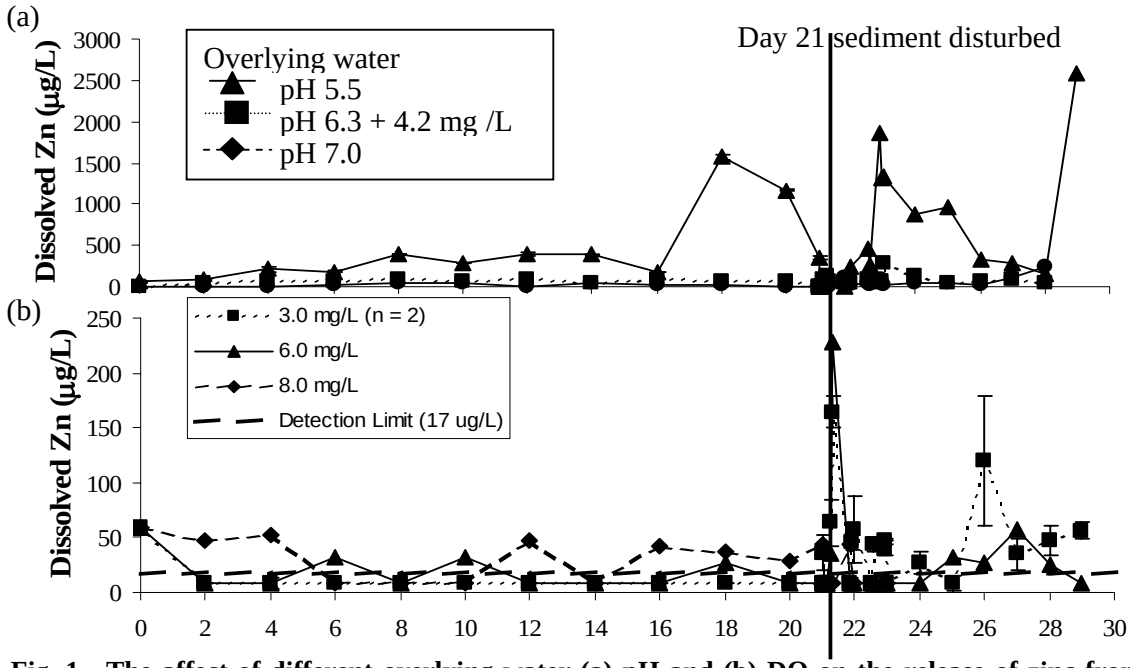

Fig. 1. The affect of different overlying water (a) pH and (b) DO on the release of zinc from contaminated marine sediments. Note the tenfold difference in concentrations between tests.

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